Electrochemistry example problems
CH102 Spring 2017 General Chemistry
Tuesday, April 25, 2017

Problem 1: At 25 °C, the standard reduction potential of Zn^{2+} is $E^{o} = -0.763$ V. A galvanic cell (voltage is positive) is made by coupling a standard Zn/Zn^{2+} electrode to a standard hydrogen electrode at 25 °C. The hydrogen electrode is then buffered to have pH = 5.57. Calculate the resulting cell potential.

The reduction potential of the standard hydrogen electrode is (by definition) exactly 0 V. Since this is greater than standard reduction potential of Zn^{2+}, $E^{o} = -0.763$ V, we conclude the following: H^+ is reduced to H_2 at the cathode, $2\ H^+(aq, 10^{-pH}\ M) + 2\ e^- \longrightarrow H_2(g, 1\ atm)$, and Zn is oxidized to Zn^{2+} at the anode, $Zn(s) \longrightarrow Zn^{2+}(aq, 1\ M) + 2\ e^-$. From these half reactions, we see that the number of electrons per reaction unit is $n_e = 2$. The full cell redox reaction is $2\ H_3O^+(aq, 10^{-pH}\ M) + Zn(s) \longrightarrow H_2(g, 1\ atm) + Zn^{2+}(aq, 1\ M) + 2\ H_2O(l)$, and therefore the we can evaluate the reaction quotient to be

$$Q = \frac{[Zn^{2+}]p_{H_2}}{[H_3O^+]^2} = \frac{1}{(10^{-pH})^2}$$

The standard cell potential is

$$E^\circ = E^\circ_{cathode} - E^\circ_{anode} = 0 - (-0.763) = +0.763\ V$$

With Q and E°, we can use the Nernst equation at 25 °C to evaluate the cell potential,

$$E = E^\circ - \frac{0.05912\ V}{n_e}\log(Q)$$

$$= 0.763\ V - \frac{0.05912\ V}{2}\log\left(\frac{1}{(10^{-pH})^2}\right)$$

$$= 0.763\ V - 0.05912\ V \times pH$$

$$= 0.763\ V - 0.05912\ V \times 5.57$$

$$= 0.434\ V$$

Problem 2: This question concerns a concentration cell with positive voltage at 25 °C, constructed from hydrogen half cells of different hydronium ion concentration and sealed so that their hydrogen gas pressure can be controlled. In one half cell the hydronium concentration is 2.0 M and the hydrogen gas pressure is 0.50 atm, and in the other half cell the hydronium concentration is 0.020 M and the hydrogen gas pressure is 5.0 atm. Platinum electrodes are used to connect the cell to an external circuit.

a. Write the line notation of the cell. Indicate for each species its concentration or pressure.

For the cell to be spontaneous, the skeleton process must be from high concentration to low concentration,

$$H_3O^+(aq, 2.0\ M) \longrightarrow H_3O^+(aq, 0.020\ M)$$

The corresponding half reactions are

$$2\ H_3O^+(aq, 2.0\ M) + 2\ e^- \longrightarrow H_2(g, 0.50\ atm) + 2\ H_2O(l), \text{ cathode}$$

$$H_2(g, 5.0\ atm) + 2\ H_2O(l) \longrightarrow 2\ H_3O^+(aq, 0.020\ M) + 2\ e^-, \text{ anode}$$

and so the line notation of the cell is

$$Pt(s)\ |\ H_2(g, 5.0\ atm)\ |\ H_3O^+(aq, 0.020\ M)\ ||\ H_3O^+(aq, 2.0\ M)\ |\ H_2(g, 0.50\ atm)\ |\ Pt(s)$$

b. Calculate the cell voltage at 25 °C

The standard potential is $E° = 0$ V. From the half reactions, the full cell reaction is

$$2\ H_3O^+(aq, 2.0\ M) + H_2(g, 5.0\ atm) \longrightarrow H_2(g, 0.50\ atm) + 2\ H_3O^+(aq, 0.020\ M)$$

From the full cell reaction, the reaction quotient is

$$Q = \frac{0.50 \times 0.020^2}{2.0^2 \times 5} = 1.0 \times 10^{-5}$$

And from the reaction quotient, the cell voltage is

$$E = E° - \frac{0.05912\ \text{V}}{n_e} \log(Q)$$

$$= 0 - \frac{0.05912\ \text{V}}{2} \log(1.0 \times 10^{-5})$$

$$= + \frac{0.05912\ \text{V}}{2} \times 5.0$$

$$= +0.15\ \text{V}$$